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Enantioselective desymmetrization of *meso*-*N*-(heteroarenesulfonyl)aziridines with $TMSN_3$ catalyzed by chiral Lewis acids

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ABSTRACT

A catalytic enantioselective desymmetrization of *meso*-*N*-(heteroarenesulfonyl)aziridines with $TMSN_3$ using chiral Lewis acids afforded products with high enantioselectivity. As proof of the utility of this procedure, the precursor of selective κ-opioid agonist (1*S*,2*S*)-(−)-U-50,488 was synthesized.

Optically active vicinal diamines are very important compounds for the synthesis of natural compounds and stereoselective catalysts. Furthermore, vicinal diamine compounds have demonstrated a range of bioactivity that includes antiparasitic [e.g., (*R*)-praziquantel, oxamniquine],[1] anticancer [(−)-quinocarcin],[2] and protease inhibitory activity.[3,4] Therefore, the stereoselective synthesis of chiral vicinal diamine compounds has received considerable attention.[5] One of the most efficient methods for the synthesis of chiral vicinal diamine precursors is the catalytic enantioselective desymmetrization of *meso*-aziridines with azide compounds. This type of reaction affords chiral β-aminoazides, which can be easily converted to chiral vicinal diamines. Although there are many reports on the enantioselective desymmetrization of *meso*-aziridines with various nucleophiles,[6] this type of reaction with azide compounds is still rare.[7] Jacobsen and co-workers pioneered the highly enantioselective desymmetrization of aziridines with $TMSN_3$ by using a chiral chromium catalyst (up to 94% ee).[7a] Recently, Shibasaki[7b] and Parquett[7d,e] reported that the ring-opening reaction of *N*-(4-nitrobenzoyl)aziridines with $TMSN_3$ using different chiral yttrium catalysts gave products with high enantioselectivity. Antilla and co-workers demonstrated that chiral phosphoric acids could be used for the ring-opening reaction of aziridines.[7c] Despite the impressive progress achieved in this reaction, expanding the scope of catalytic enantioselective desymmetrization of aziridines with respect to both the chiral catalyst and the substrate would be highly desirable. Although the *N*-sulfonyl group certainly enhances the reactivity of the ring-opening reaction of aziridines to attack an azide, to our knowledge, there are no reports on the enantioselective desymmetrization of *N*-(arenesulfonyl)aziridines with an azide. Recently, we[8] and others[9] have developed novel bifunctional coordinative heteroarenesulfonyl groups whose conformations and reactivities can be controlled by chelation with chiral Lewis acids or organocatalysts. Herein, we report the catalytic enantioselective desymmetrization of *meso*-aziridines having a heteroarenesulfonyl group with $TMSN_3$ using chiral Lewis acids prepared from commercially available bis(oxazoline) ligands (Fig. 1).

We examined the enantioselective desymmetrization of *meso*-*N*-(heteroarenesulfonyl)aziridines **1a–g**[10] by using a catalytic amount of chiral Lewis acids prepared from various bis(oxazoline)s

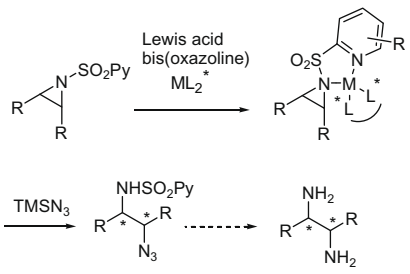

Figure 1. Catalytic enantioselective ring-opening reaction of *meso*-*N*-(2-pyridinesulfonyl)aziridines with $TMSN_3$.

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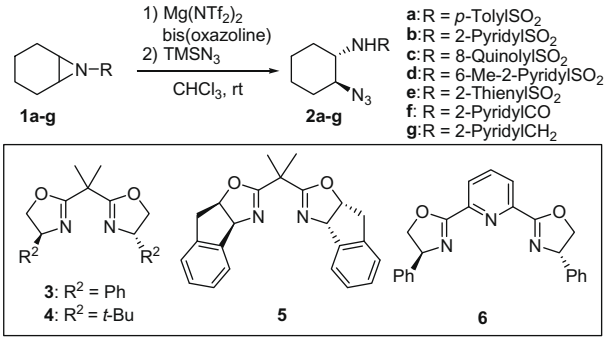
Table 1
Enantioselective desymmetrization of *N*-(heteroarenesulfonyl)aziridines **1a–g** with $TMSN_3$ in the presence of various chiral Lewis acids[a]



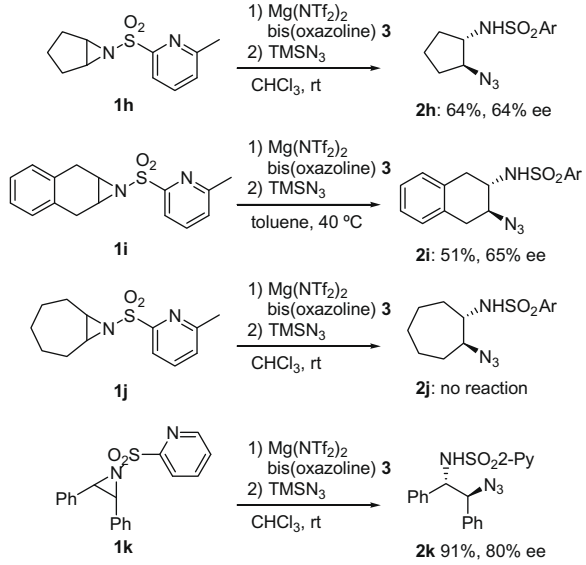
Run	1	Ligand	2	Yield (%)	Ee[b] (%)
1	**1a**	**3**	**2a**	Trace	—
2	**1b**	**3**	**2b**	98	70(*S*)
3	**1c**	**3**	**2c**	67	60
4	**1d**	**3**	**2d**	63	85(*S*) (99)[c]
5	**1e**	**3**	**2e**	Trace	—
6	**1f**	**3**	**2f**	99	11
7	**1g**	**3**	**2g**	Trace	—
8	**1d**	**4**	**2d**	12	0
9	**1d**	**5**	**2d**	52	39
10	**1d**	**6**	**2d**	Trace	—

[a] $Mg(NTf_2)_2$ (0.1 equiv), bis(oxazoline) (0.2 equiv), and $TMSN_3$ (3.0 equiv) were used.
[b] Ee was determined by HPLC analysis using chiral columns.
[c] Ee obtained after single recrystallization from toluene is shown in parenthesis.

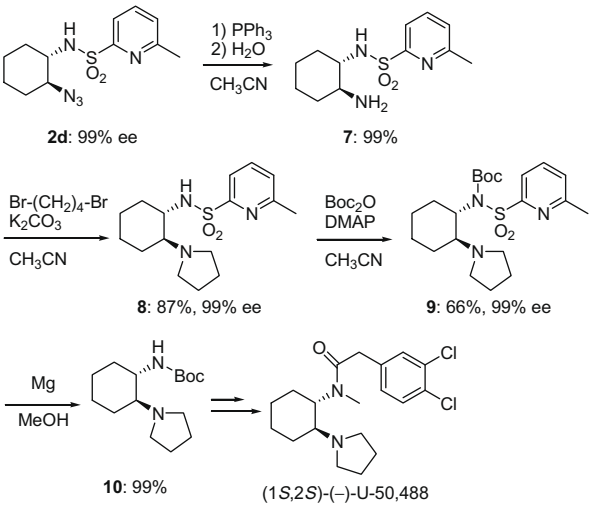
3–6 and $Mg(NTf_2)_2$. The results are shown in Table 1. The reaction of *N*-(*p*-toluenesulfonyl)aziridine **1a** with $TMSN_3$ using $Mg(NTf_2)_2$/Box-Ph **3** as a chiral Lewis acid catalyst did not afford product **2a**, whereas *N*-(2-pyridinesulfonyl)- and *N*-(8-quinolinesulfonyl)aziridines **1b**, **c** afforded products **2b**, **c** with good enantioselectivity (entries 1–3). Interestingly, *N*-(6-methyl-2-pyridinesulfonyl)aziridine **1d** showed higher enantioselectivity than **1b** (entry 4). The reaction of *N*-(2-thiophenesulfonyl)aziridine **1e** did not afford product **2e** in good yield (entry 5). The reaction of *N*-picolyl- and *N*-pyridylmethyl-substituted aziridine **1f**, **g** did not afford good results (entries 6 and 7). After optimization of chiral Lewis acids derived from other Box ligands such as Box-*t*Bu **4**, indaBox **5**, and Pybox **6**, we found $Mg(NTf_2)_2$/**3** to be an efficient chiral Lewis acid for asymmetric desymmetrization of **1d** (entries 8–10).[11,12] Recrystallization of (*S*)-**2d** (85% ee) from toluene afforded enantiomerically pure (*S*)-**2d** (entry 4).

With these optimized condition, the ring-opening reaction of **1h, i** afforded the products **2h, i** in good yield with moderate enantioselectivity, although the reaction of **1j** did not afford the product **2j** (Scheme 1). Furthermore, acyclic aziridine **1k** using $Mg(NTf_2)_2$/**3** afforded product **2k** in high yield with good enantioselectivity .

To assess the synthetic potential of this stereoselective preparation of chiral vicinal diamines, we tried to prepare U-50,488, which has been reported to be a highly selective κ-opioid agonist free from the adverse side effects of μ-opioid agonists like morphine.[13] The pharmacological activities of U-50,488 are related to the configuration of its stereogenic centers. (1*S*,2*S*)-(−)-U-50,488 exhibits greater κ agonist activity than its enantiomer and *cis* diastereomers.[14] Therefore, the stereoselective synthesis of (1*S*,2*S*)-U-50,488 is important. However, to our knowledge, there is no report on the enantioselective synthesis of U-50,488 through the catalytic enantioselective ring-opening reactions of aziridines.[15] Reduction of azide group of **2d** by triphenylphosphine yielded N-sulfonylated



Scheme 1. Enantioselective ring-opening reaction of **1h–k**.



Scheme 2. Synthesis of (1*S*,2*S*)-U-50,488.

diamine **7**, which was successfully alkylated by 1,4-dibromobutane to give the pyrrolidine derivative **8** in high yield (Scheme 2).[16] The sulfonamide group of **8** was protected by Boc_2O, after which the 6-methyl-2-pyridinesulfonyl group was removed by magnesium in MeOH[17] to give the *N*-Boc amide **10** in high yield. The *N*-Boc amide **10** would be transformed to enantiomerically pure U-50,488.[15a]

The enantioselective desymmetrization of *N*-(2-pyridinesulfonyl)aziridines **1b, d** with $TMSN_3$ gave products **2b, d** in good yield with good enantioselectivity, whereas the reaction of *N*-(*p*-toluenesulfonyl)aziridine **1a** did not afford the product. This result shows that the 2-pyridinesulfonyl group acts as an efficient activating group. Assuming that Mg(II) forms a tetrahedral bidentate-coordinating complex with the substrate,[18] the presumed structure of most reactive complex **1d**-Mg(II)/**3** is shown in Figure 2, where two Box nitrogens, one pyridyl nitrogen, and aziridine nitrogen coordinate to Mg(II). In this structure, the pyridyl group in **1d** plays an important role in stabilizing the chelation structure. Thus, $TMSN_3$ approaches aziridine avoiding steric repul-

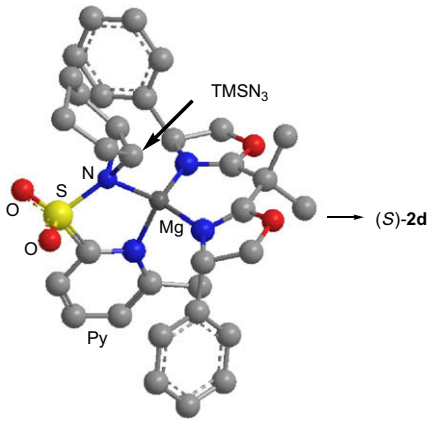


Figure 2. Presumed reaction model of **1d**-Mg(II)/**3**.

sion with the phenyl group in Box-Ph **3**, therefore (*1S,2S*)-**2d** is preferably formed.

In conclusion, the enantioselective desymmetrization of *N*-(2-pyridinesulfonyl)aziridines in the presence of $Mg(NTf_2)_2$/**3** afforded chiral β-aminoazides with good enantioselectivity. The 2-pyridinesulfonyl group works as an efficient activating group for the ring-opening reaction of aziridines. To our knowledge, this result is the first example for the enantioselective desymmetrization of *N*-(arenesulfonyl)aziridines with an azide. As a proof of the utility of this procedure, the precursor of enantiomerically pure (1*S*,2*S*)-(−)-U-50,488, which is a selective κ-opioid agonist, was synthesized.

Acknowledgments

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11. Other chiral Lewis acids derived from $Mg(OTf)_2$, CuOTf, $Cu(OTf)_2$, and $Zn(OTf)_2$ with **3** afforded product **2d** with lower enantioselectivity than that using $Mg(NTf_2)_2$/**3**.
12. We also examined the reaction in CH_2Cl_2, $ClCH_2CH_2Cl$, toluene, Et_2O, and CH_3CN, giving the product **2d** with lower enantioselectivity than that in $CHCl_3$.
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16. *Typical procedure for the asymmetric desymmetrization of* **1d** using the catalyst $Mg(NTf_2)_2$/**3** (Table 1, entry 4). To a solution of $Mg(NTf_2)_2$ (4.6 mg, 7.9 μmol) and **3** (5.5 mg, 0.016 mmol) in $CHCl_3$ (0.8 mL), **1d** (20 mg, 0.079 mmol) in $CHCl_3$ (0.2 mL) was added and stirred for 1 h. Then, $TMSN_3$ (31 μl, 0.24 mmol) was added at room temperature. The reaction mixture was stirred for 63 h. Water (1.0 mL) was added and the mixture was stirred for 10 min at room temperature. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by chromatography (benzene/ethyl acetate = 90:10) to afford **2d** (14.7 mg, 63%, 85% ee) as a white solid; $[\alpha]_D^{25}$ +56.0 (*c* 0.42, $CHCl_3$, 99% ee); mp 106.5–107.0 °C; R_f = 0.15 (benzene/ethyl acetate = 90:10); ^{1}H NMR ($CDCl_3$) δ 1.20–1.50 (m, 4H), 1.50–1.80 (m, 2H), 2.00–2.20 (m, 2H), 2.63 (s, 3H, *CH*$_3$), 3.00–3.20 (m, 2H, *CH*), 5.17–5.21 (br, 1H, *NH*), 7.29–7.35 (m, 1H, *Py*), 7.72–7.84 (m, 2H, *Py*); ^{13}C NMR ($CDCl_3$) δ 23.5, 23.8, 24.3, 30.1, 31.2, 56.8, 63.7, 118.9, 126.5, 137.9, 157.1, 159.9; IR (KBr) 3253, 2941, 2858, 2099 (N_3), 1451, 1332 (SO_2) cm^{-1}; MS(APCI) *m*/*z* 268.1 [M+H–N_2], 296.1 [M+H]; HPLC (CHIRALPAK® OD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min) t_R 11.4 (minor), t_S 19.1 (major) min.
Compound **7**: $[\alpha]_D^{25}$ +16.7 (*c* 0.41, MeOH, 99% ee); mp 145.0–147.0 °C; R_f = 0.11 (CH_2Cl_2/MeOH = 90:10); ^{1}H NMR ($CDCl_3$) δ 1.05–1.40 (m, 4H), 1.55–1.75 (m, 2H), 1.80–2.10 (m, 2H), 2.10–2.60 (br, 2H, *NH*$_2$), 2.39–2.49 (m, 1H, *CH*), 2.62 (s, 3H, *CH*$_3$), 2.80–2.95 (m, 1H, *CH*), 7.30–7.33 (m, 1H, *Py*), 7.72–7.84 (m, 2H, *Py*); ^{13}C NMR ($CDCl_3$) δ 24.2, 24.7, 25.0, 32.9, 34.8, 55.0, 61.1, 119.0, 126.4, 137.9, 157.5, 159.6; IR (KBr) 3354, 3035, 2936, 2861, 1591, 1452, 1314 (SO_2) cm^{-1}; MS(ESI) *m*/*z* 270.1 [M+H].
Compound **8**: $[\alpha]_D^{25}$ +54.6 (*c* 0.43, MeOH, 99% ee); mp 153.0–155.5 °C; R_f = 0.20 (CH_2Cl_2/MeOH = 90:10); ^{1}H NMR ($CDCl_3$) δ 1.00–1.40 (m, 4H), 1.60–1.80 (m, 7H), 2.25–2.60 (m, 7H), 2.62 (s, 3H, *CH*$_3$), 2.70–2.90 (m, 1H), 7.29–7.33 (m, 1H, *Py*), 7.72–7.86 (m, 2H, *Py*); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.4, 24.0, 24.1, 24.7, 32.4, 46.4, 55.1, 61.5, 119.6, 126.3, 137.6, 156.2, 159.6; IR (KBr) 3207, 2931, 2860, 2810, 1591, 1452, 1343 (SO_2) cm^{-1}; MS(ESI) *m*/*z* 324.2 [M+H]; HPLC (CHIRALPAK® OD-H, hexane/*i*-PrOH = 90:10, 0.5 mL/min) t_R 15.1 (minor), t_S 16.3 (major) min.
Compound **9**: $[\alpha]_D^{25}$ +57.2 (*c* 0.47, MeOH, 99% ee); mp 88.0–91.0 °C; R_f = 0.30 (AcOEt); ^{1}H NMR ($CDCl_3$) δ 1.20–1.40 (m, 4H), 1.26 (s, 9H, *CH*$_3$), 1.60–1.70 (m, 4H), 1.70–1.85 (m, 2H), 1.90–2.40 (m, 4H), 2.59 (s, 3H, *CH*$_3$), 2.70–2.90 (m, 2H), 3.45–4.60 (m, 1H, *CH*),4.20–4.34 (m, 1H, *CH*), 7.27–7.31 (m, 1H, *Py*), 7.68–7.76 (m, 1H, *Py*), 7.99–8.02 (m, 1H, *Py*); ^{13}C NMR ($CDCl_3$) δ 13.9, 23.6, 24.0, 25.1, 25.3, 27.5, 31.0, 46.9, 57.9, 61.4, 119.8, 126.1, 137.2, 150.5, 157.4, 158.9; IR (KBr) 2932, 2855, 2791, 1733, 1591, 1456, 1342 (SO_2) cm^{-1}; MS(ESI) *m*/*z* 424.3 [M+H]; HPLC (CHIRALPAK® OD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min) t_S 5.3 (major), t_R 6.0 (minor) min.

Compound **10**: $[\alpha]_D^{25}$ +33.1 (*c* 0.21, MeOH, 99% ee); R_f = 0.10 (CH_2Cl_2/MeOH = 90:10); ^1H NMR ($CDCl_3$) δ 1.10–1.50 (m, 4H), 1.45 (s, 9H, CH_3), 1.55–1.85 (m, 8H), 2.30–1.70 (m, 5H), 3.20–3.40 (m, 1H, *CH*), 5.25 (br, 1H, *NH*); MS(ESI) *m*/*z* 269.3 [M+H].

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18. A tetrahedral Mg(II) complex has been proposed, see: (a) Corey, E. J.; Ishihara, K. *Tetrahedron Lett.* **1992**, *33*, 6807–6810; (b) Sibi, M. P.; Sausker, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 984–991; An octahedral structure has been also proposed: (c) Sibi, M. P.; Petrovic, G.; Zimmerman, J. *J. Am. Chem. Soc.* **2005**, *127*, 2390–2391; (d) Gothelf, K. V.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **1998**, *63*, 5483–5488.